When is a Peak a Peak?

and Other Uses of Signal-to-Noise Ratios in μ-XRF Analysis

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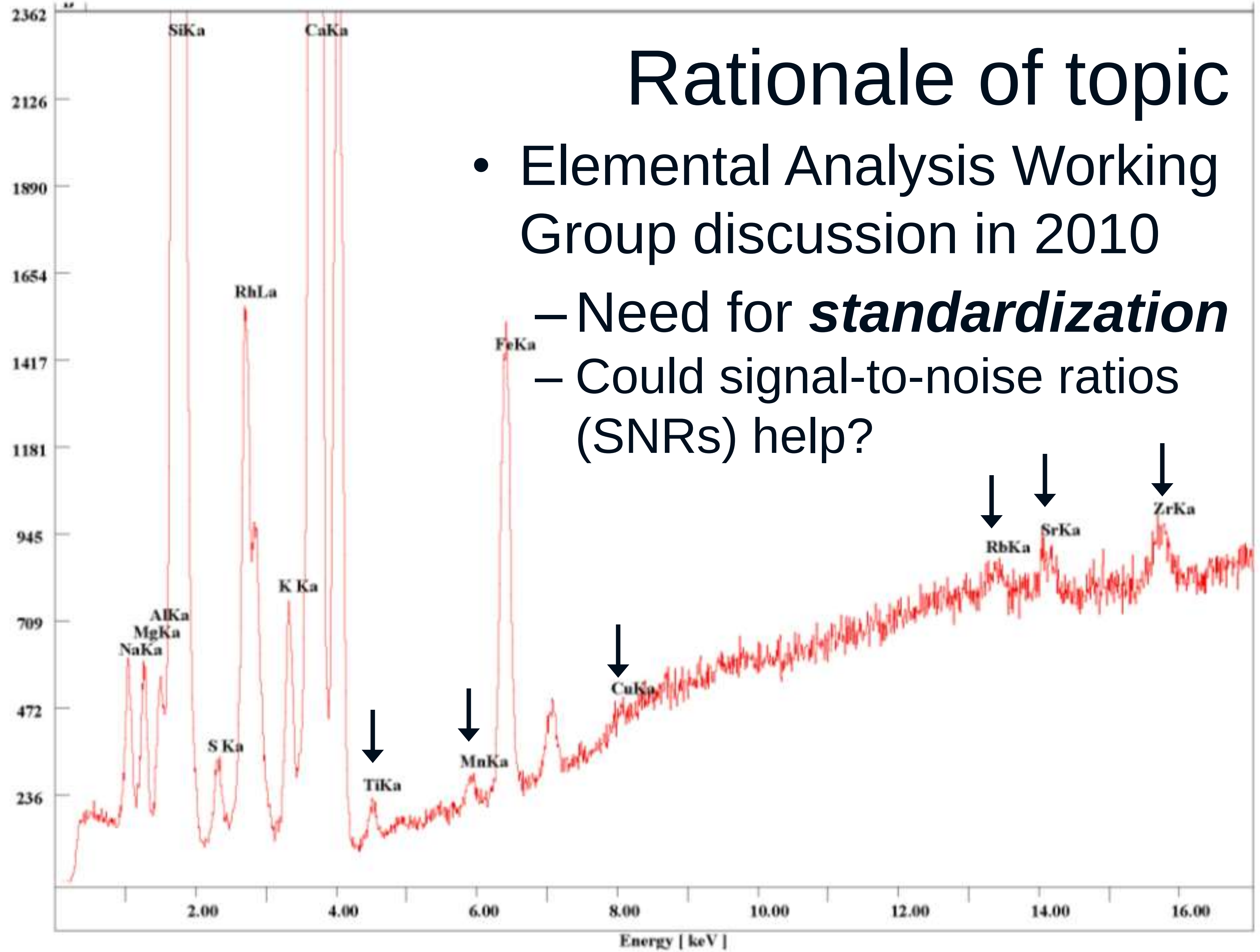
Rationale of topic

- Elemental Analysis Working Group discussion in 2010
  - Need for ***standardization***
  - Could signal-to-noise ratios (SNRs) help?



Overview of presentation

- Definitions of terms
- Reasons to calculate signal-to-noise ratios
- How to calculate signal-to-noise ratios

CAUTION: STATISTICS AHEAD

The contents on the following pages contain numerical information and descriptions that are known by the State of Michigan to cause headaches, blurred vision, and disrupted sleep patterns.

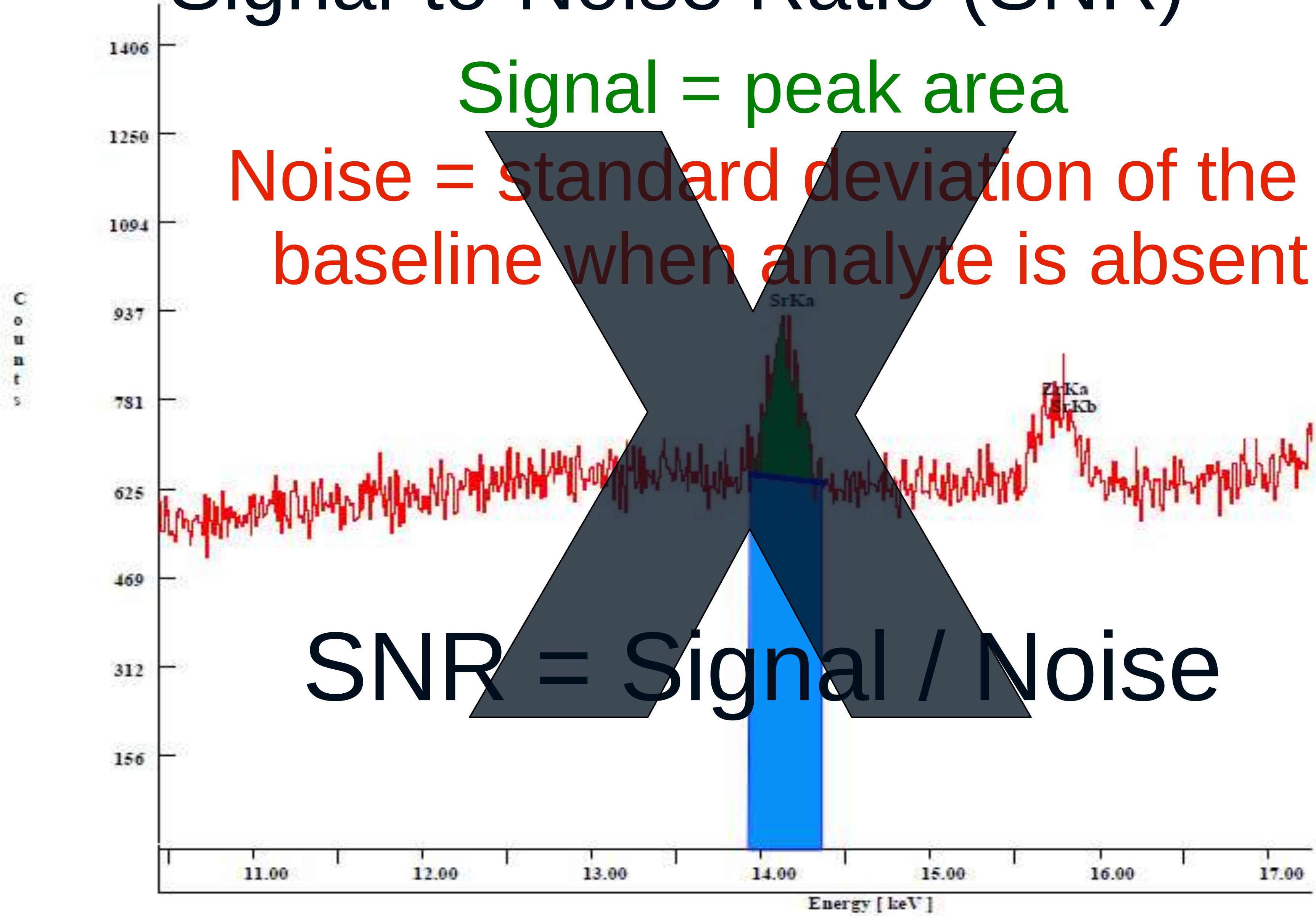
Definitions:

Signal-to-Noise Ratio (SNR)

Signal = peak area

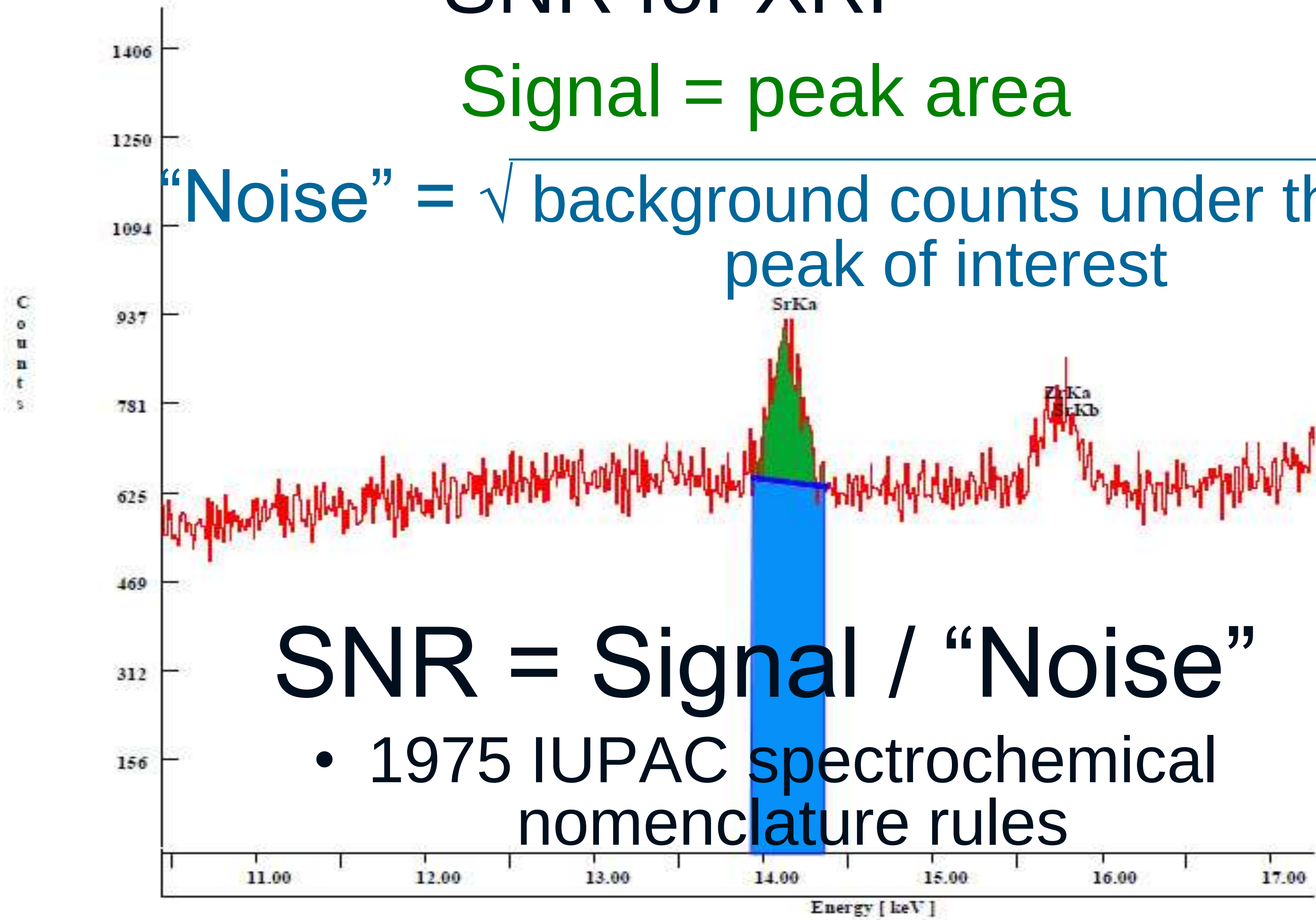
Noise = standard deviation of the baseline when analyte is absent

SNR = Signal / Noise



Definitions:

SNR for XRF



Signal = peak area

"Noise" = $\sqrt{\text{background counts under the peak of interest}}$

SNR = Signal / "Noise"

- 1975 IUPAC spectrochemical nomenclature rules

Definitions:
Limit of Detection (LOD)

Lowest concentration of an analyte that can be ***reliably detected***

LOD: SNR = 3

- 1975 IUPAC nomenclature rules;
  1980 ACS paper in *Analytical Chemistry*
- ~90% confidence level that the analyte is present

DEFINITIONS:
Limit of Quantitation (LOQ)

Lowest concentration of an analyte that can be ***reliably quantified***

LOQ: SNR = 10

- 1980 ACS paper

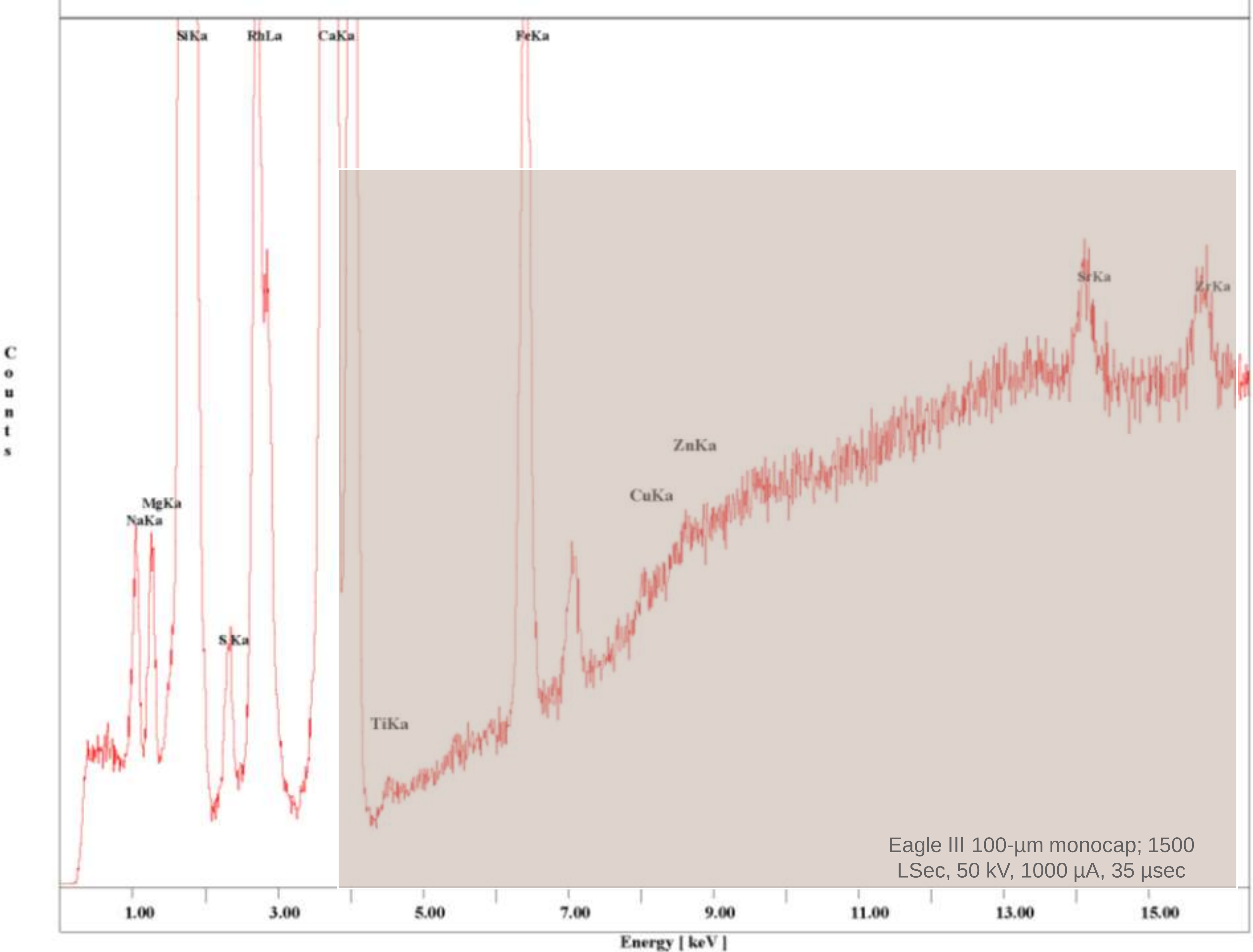
Reasons to calculate SNRs

#1: When is a peak a peak?

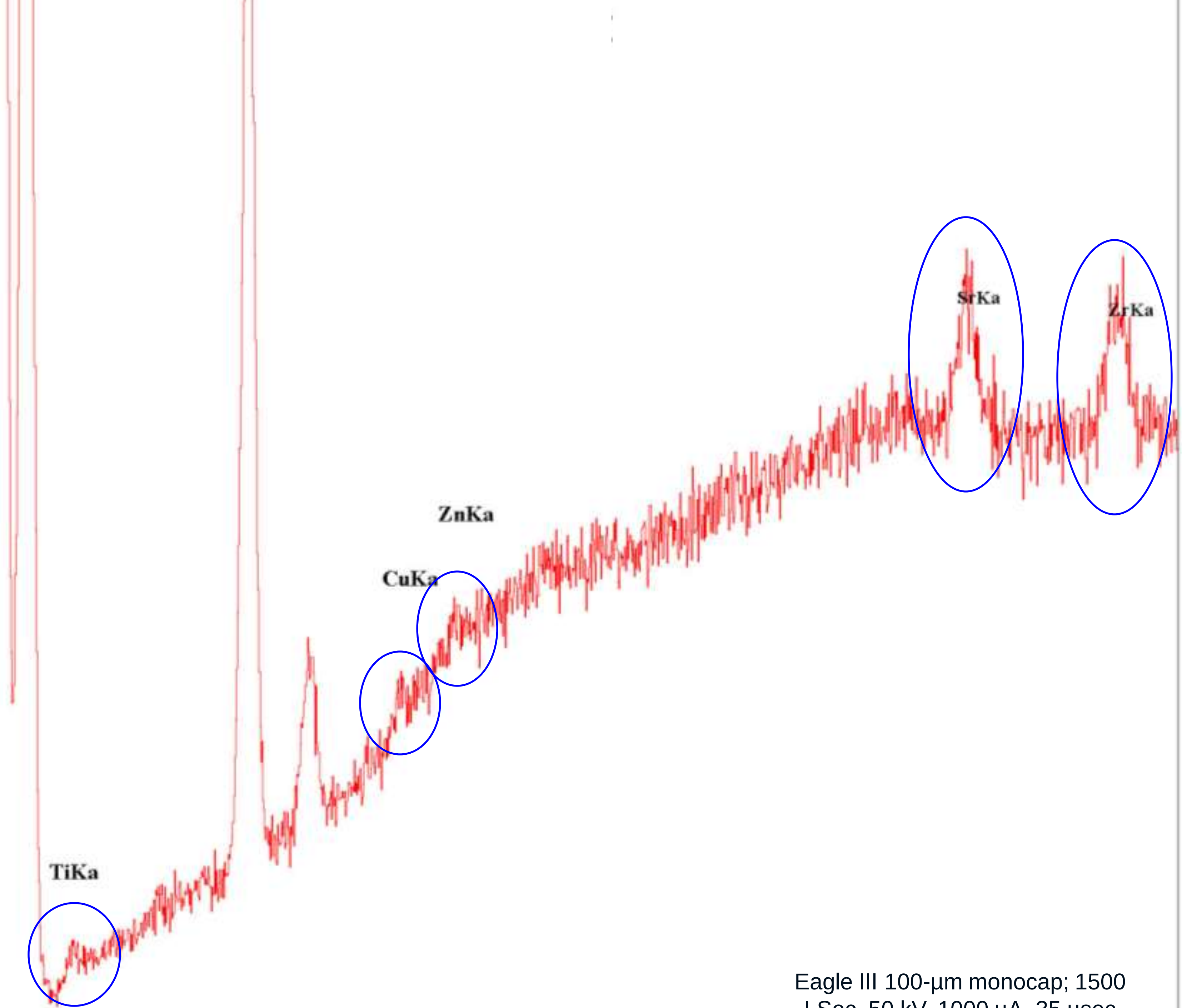
- Peak labels
  - 1975 IUPAC rules:

    SNR ≥3: peak

  - Caveat 1: Cr, Cu, Zn
  - Caveat 2: shoulder peaks
  - Caveat 3: Interference from other elements



SiKa
RhLa
CaKa
FeKa
SrKa
ZrKa
ZnKa
CuKa
MgKa
NaKa
S Ka
TiKa
Eagle III 100-µm monocap; 1500 LSec, 50 kV, 1000 µA, 35 µsec
Counts
1.00
3.00
5.00
7.00
9.00
11.00
13.00
15.00
Energy [keV]



Eagle III 100-µm monocap; 1500 LSec, 50 kV, 1000 µA, 35 µsec

Reasons to calculate SNRs

#2: Should I use it in a ratio?

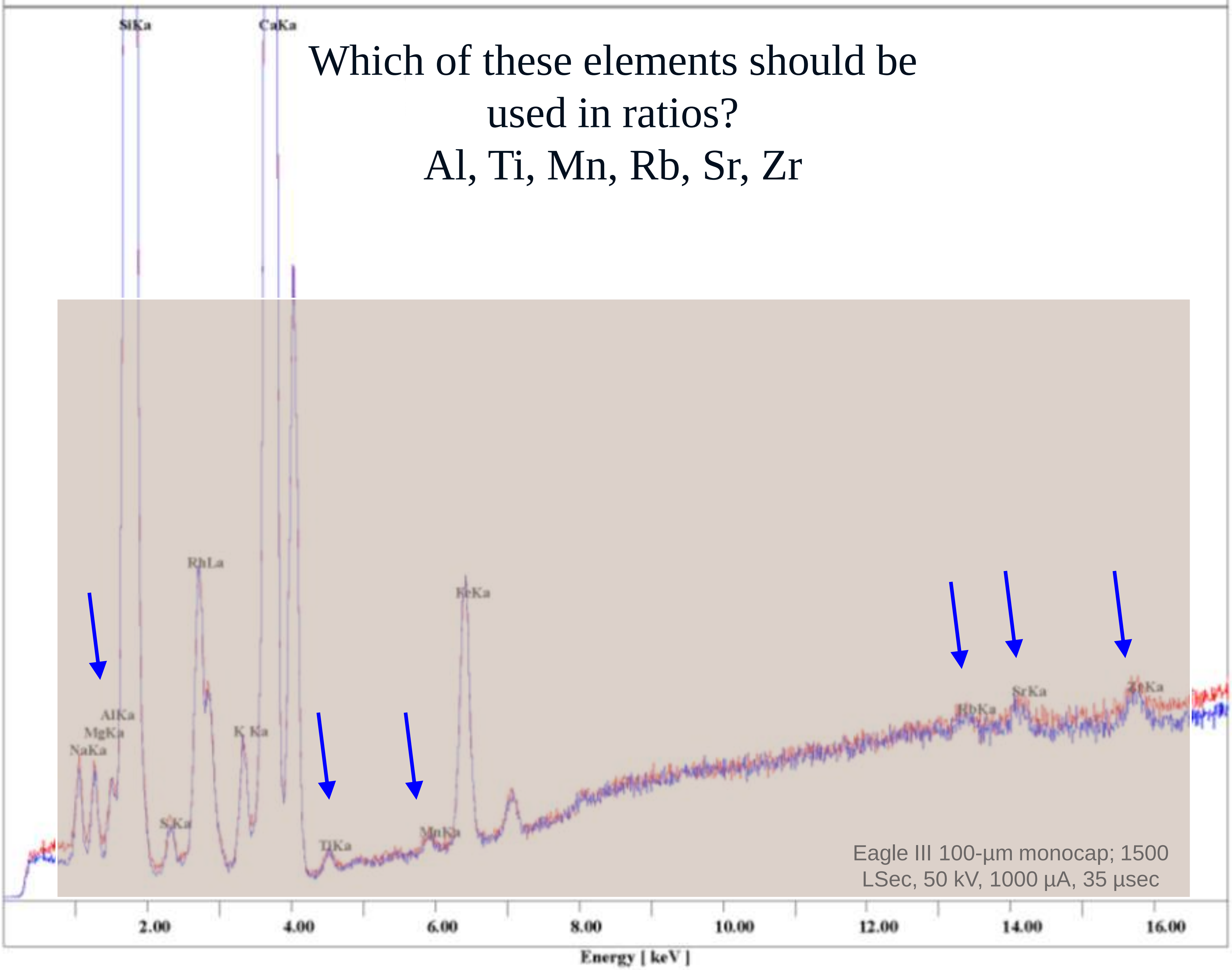
- Selection of elements for ratio comparisons
  - Application of 1980 ACS Guidelines

    LOQ: SNR of 10 (reliably quantified)

    SNR ≥ 10 may be used for ratios

  - Same caveats apply

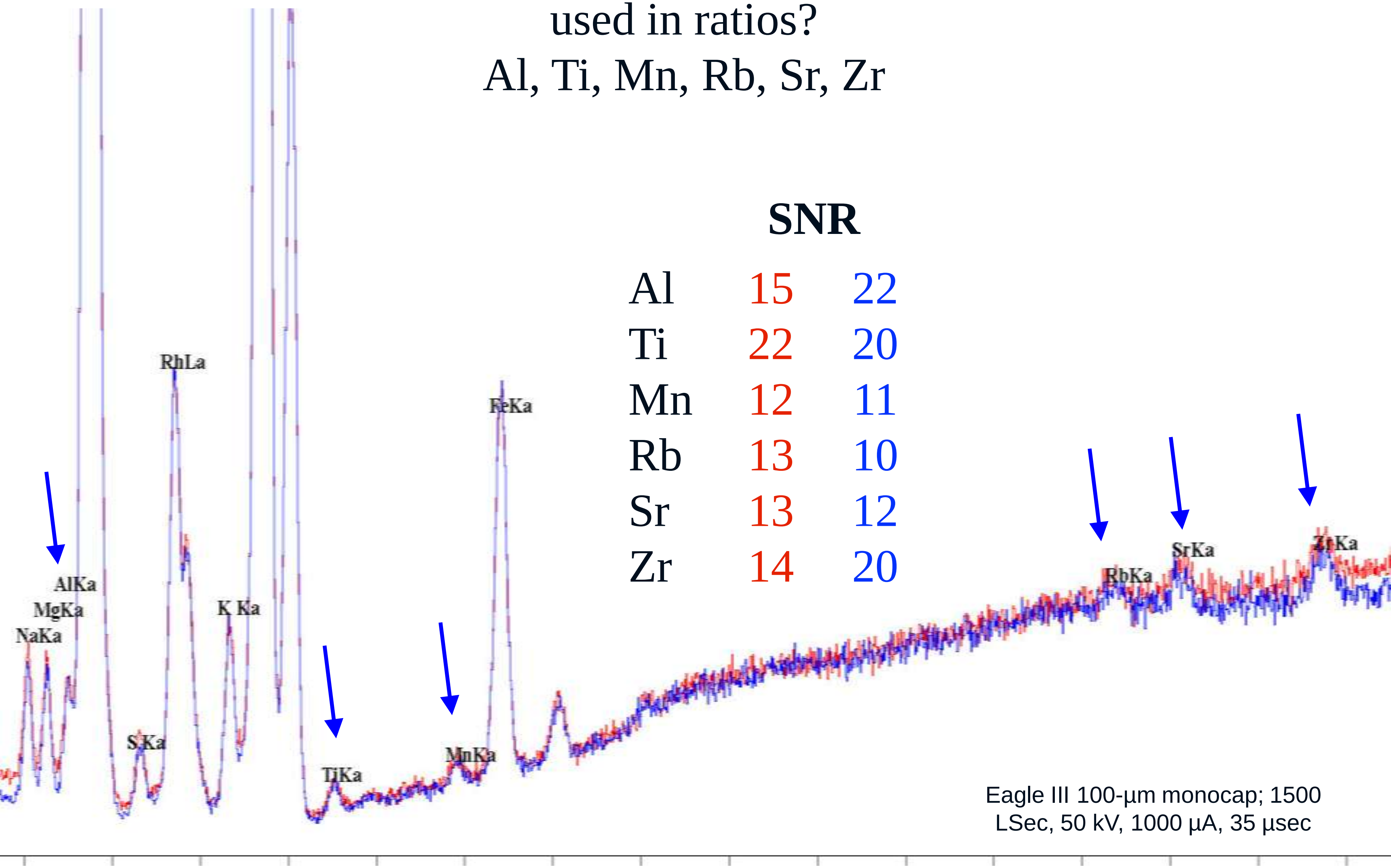
Which of these elements should be used in ratios?
Al, Ti, Mn, Rb, Sr, Zr



Which of these elements should be used in ratios?
Al, Ti, Mn, Rb, Sr, Zr

SNR

Al	15	22
Ti	22	20
Mn	12	11
Rb	13	10
Sr	13	12
Zr	14	20



Reasons to calculate SNRs

#3: How low can you go?

- Estimate limits of detection in standard glasses

$$\text{LOD (ppm)} = \frac{3 \cdot \text{given concentration (ppm)}}{\text{SNR}}$$

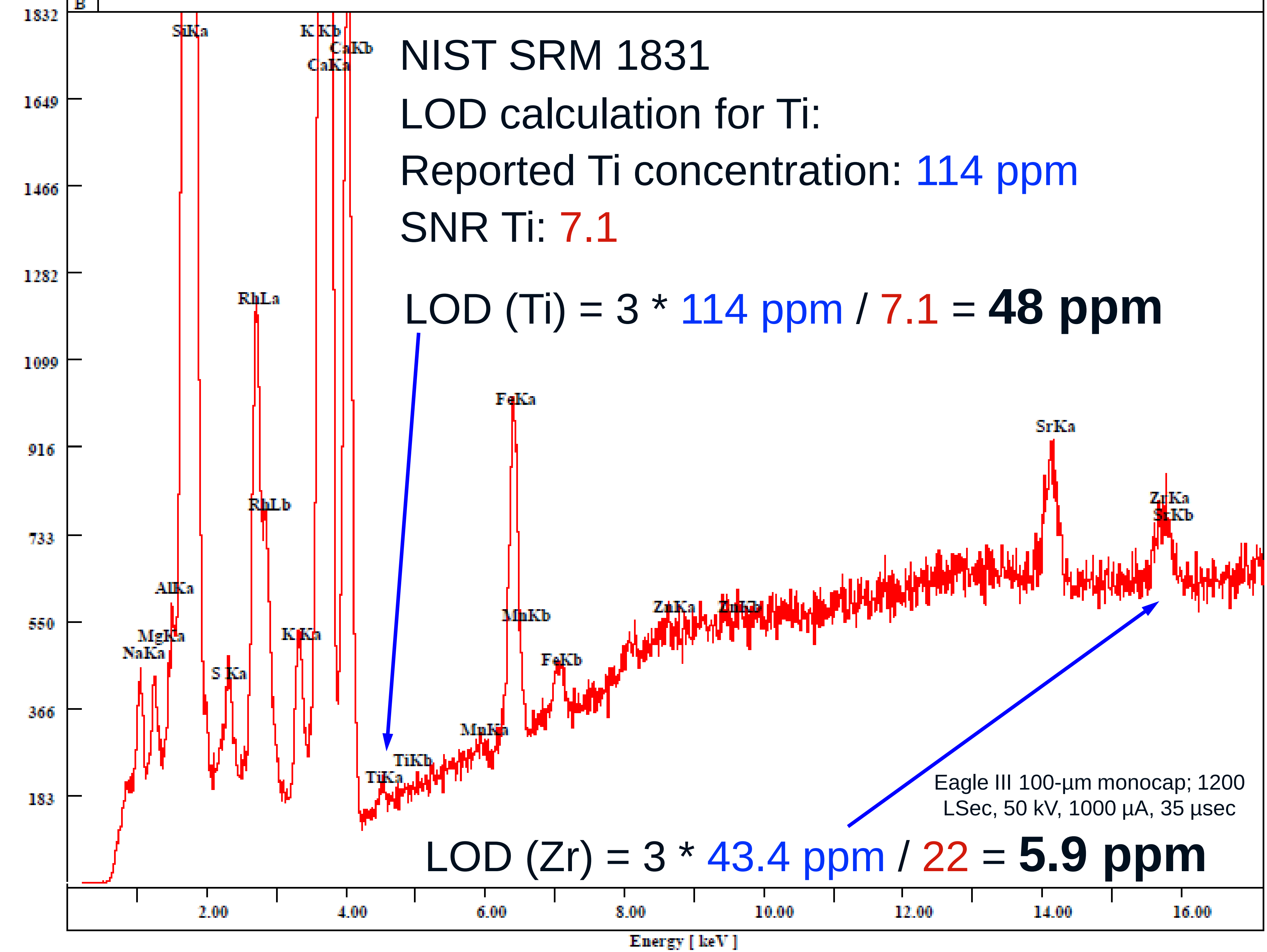
NIST SRM 1831

LOD calculation for Ti:

Reported Ti concentration: 114 ppm

SNR Ti: 7.1

LOD (Ti) = 3 * 114 ppm / 7.1 = **48 ppm**



Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

LOD (Zr) = 3 * 43.4 ppm / 22 = **5.9 ppm**

Average LODs of three glass standards
NIST 1831, FGS-1, FGS-2

Elem	*LOD (ppm)*
Na	*6979*
Mg	*1587*
Al	*854*
K	*129*
Ca	*60*
Ti	*28*
Mn	*17*
Fe	*14*
Rb	*7.0*
Sr	*7.0*
Zr	*5.3*

(100-µm monocap, 1200 LSec)

Reasons to calculate SNRs

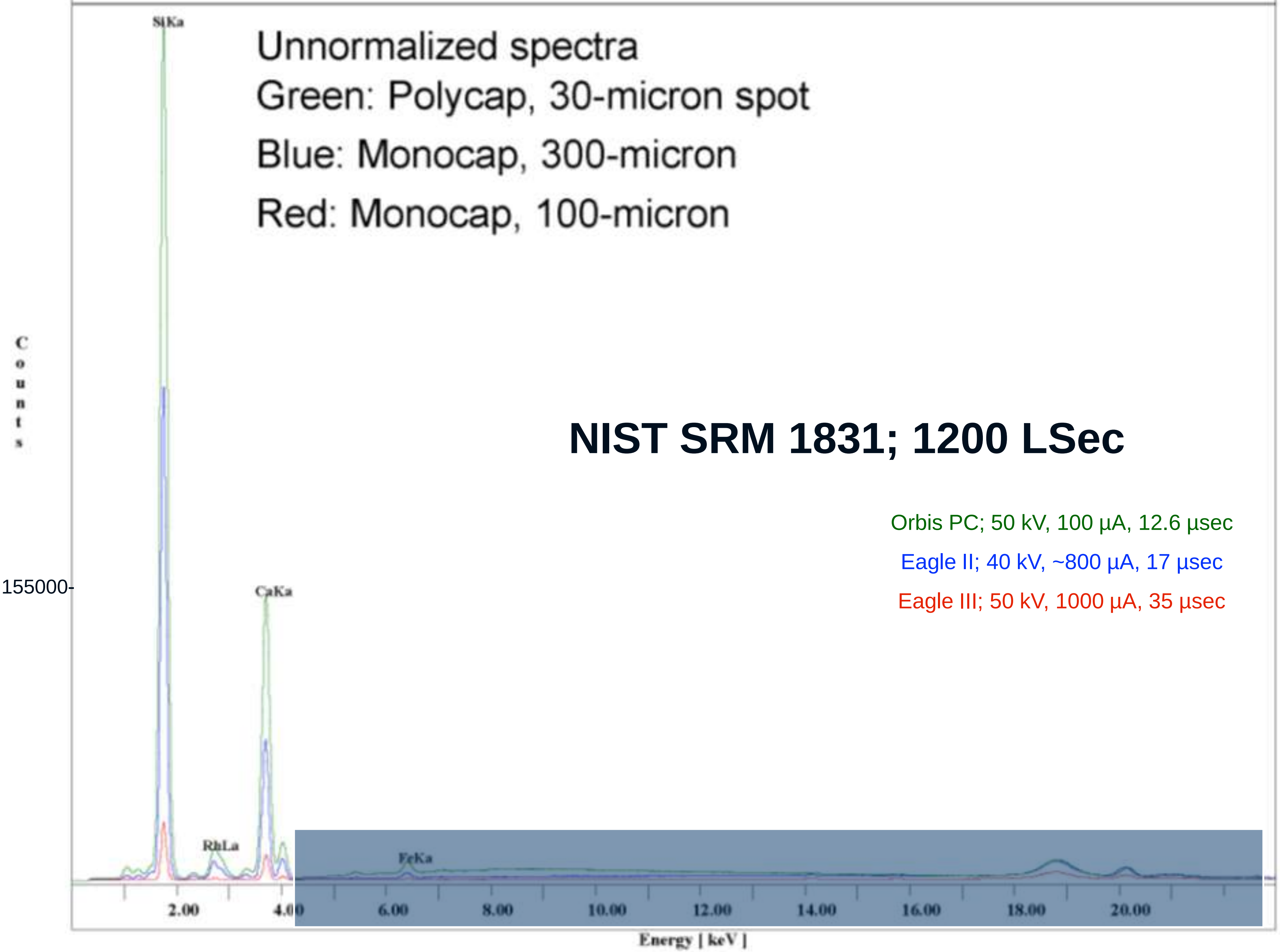
#4: How do XRF systems compare?

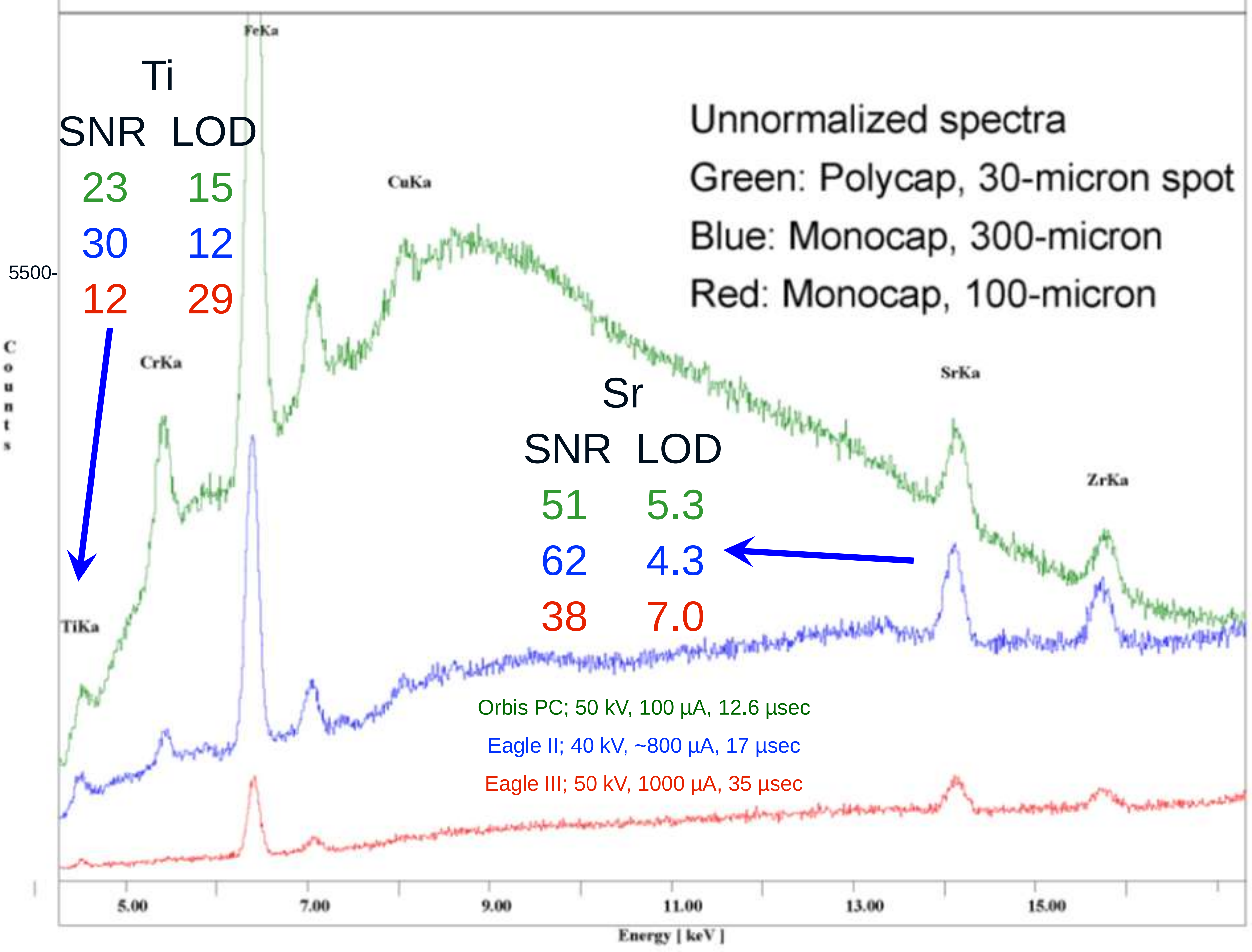
- Compare LODs of standard glass samples run on different instruments

LODs (ppm) for three different configurations

	A Monocap, 100 µm	B Polycap, 30-um spot	C Monocap, 300 µm
Mg	1521	697	633
Al	874	n/a	445
K	138	57	62
Ca	59	16	29
Ti	29	15	12
Fe	14	6.0	8.3
Rb	5.0	4.1	3.6
Sr	7.0	5.3	4.3
Zr	5.1	3.7	3.2

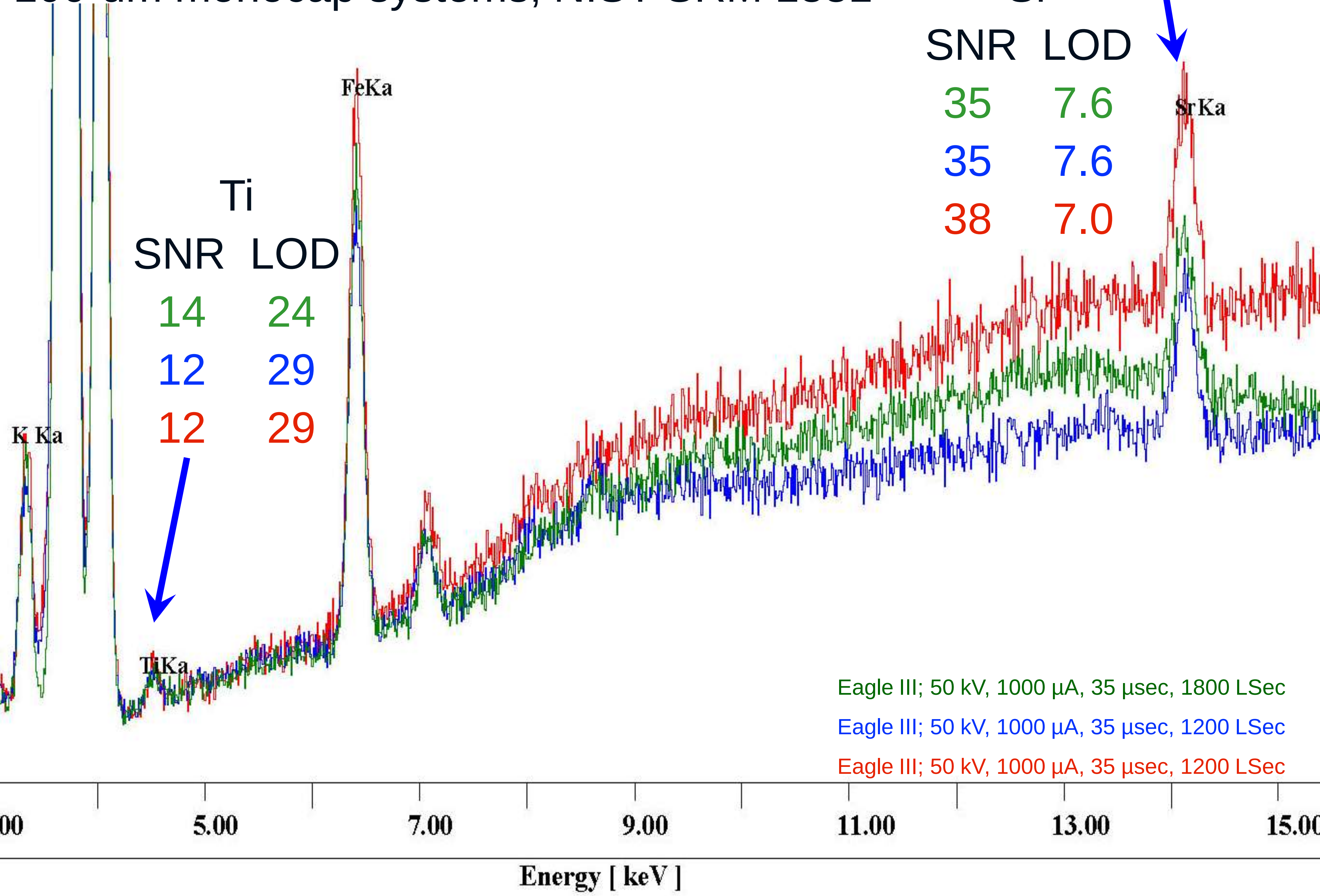
(NIST SRM 1831; 1200 LSec)


Unnormalized spectra
Green: Polycap, 30-micron spot
Blue: Monocap, 300-micron
Red: Monocap, 100-micron
NIST SRM 1831; 1200 LSec
Orbis PC; 50 kV, 100 µA, 12.6 µsec
Eagle II; 40 kV, ~800 µA, 17 µsec
Eagle III; 50 kV, 1000 µA, 35 µsec
SiKa
CaKa
RhLa
FeKa
Counts
155000-
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
18.00
20.00
Energy [keV]



Ti
SNR LOD
23 15
30 12
12 29
FeKa
CuKa
CrKa
TiKa
5500-
Counts
Unnormalized spectra
Green: Polycap, 30-micron spot
Blue: Monocap, 300-micron
Red: Monocap, 100-micron
Sr
SNR LOD
51 5.3
62 4.3
38 7.0
SrKa
ZrKa
Orbis PC; 50 kV, 100 µA, 12.6 µsec
Eagle II; 40 kV, ~800 µA, 17 µsec
Eagle III; 50 kV, 1000 µA, 35 µsec
5.00
7.00
9.00
11.00
13.00
15.00
Energy [keV]

100-um monocap systems, NIST SRM 1831



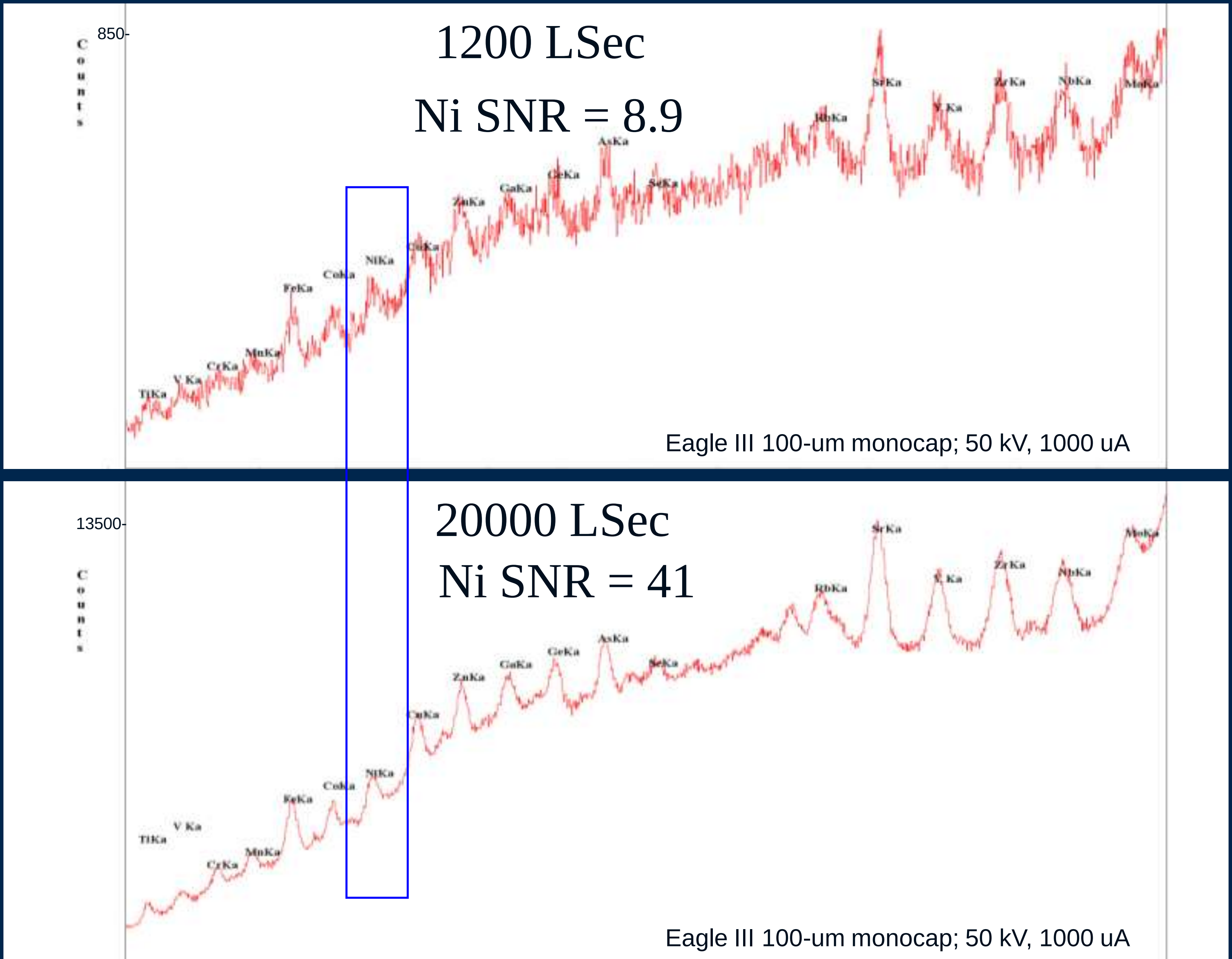
Reasons to calculate SNRs

#5: QA/QC

- Validation (instrument or method)
  - SNR target: NIST SRM 612 elements ≥ 10
- Daily function verification
  - LOD target: Ti ≥ 50 ppm

    [LOD of 50 ppm for Ti corresponds to SNR of 6.8 in NIST SRM 1831]

SRM 612 (nominal 50 ppm)



Usefulness of SNRs

- When is a peak a peak?

  SNR = 3
- When to use a peak in a ratio?

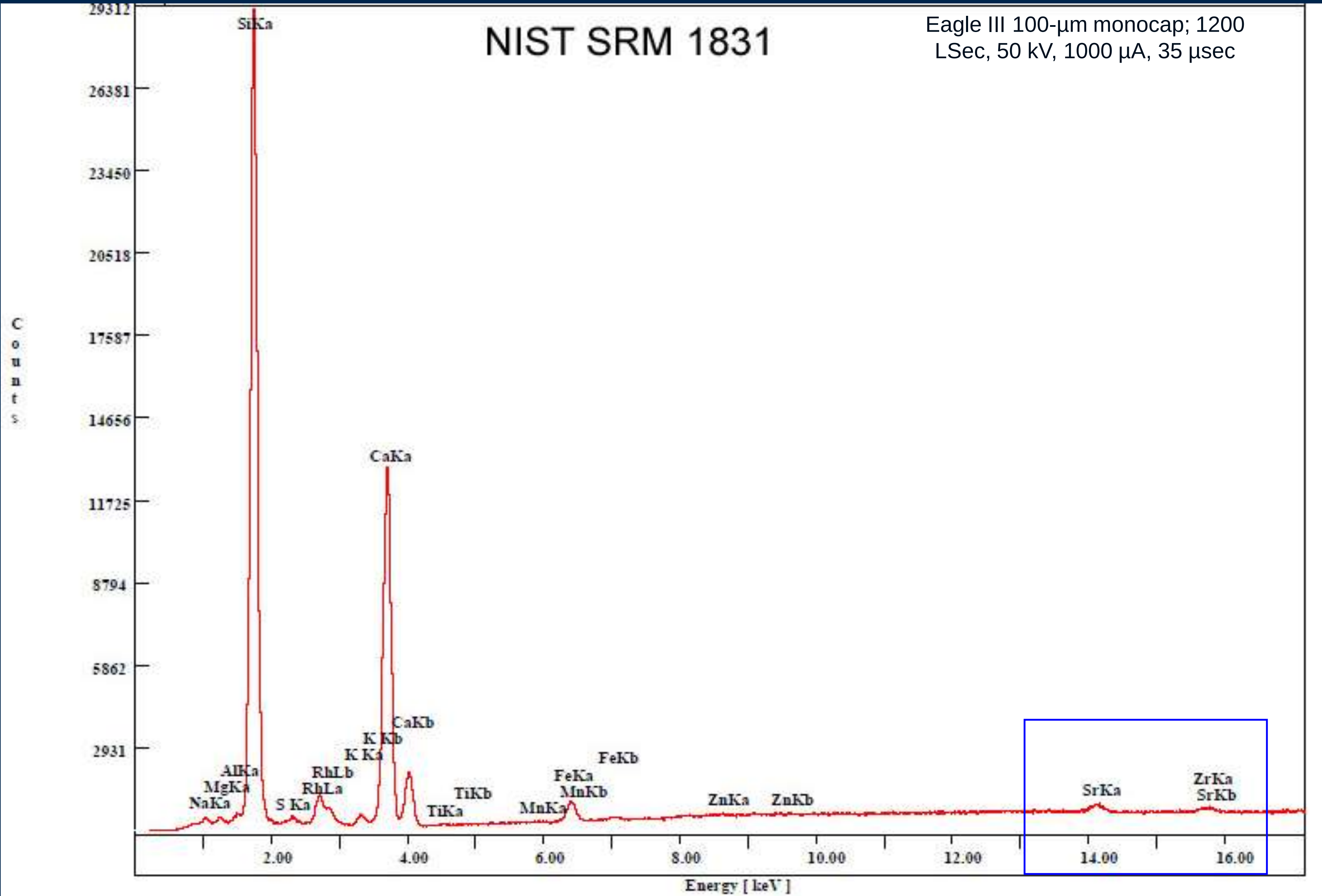
  SNR = 10
- How low can you go?

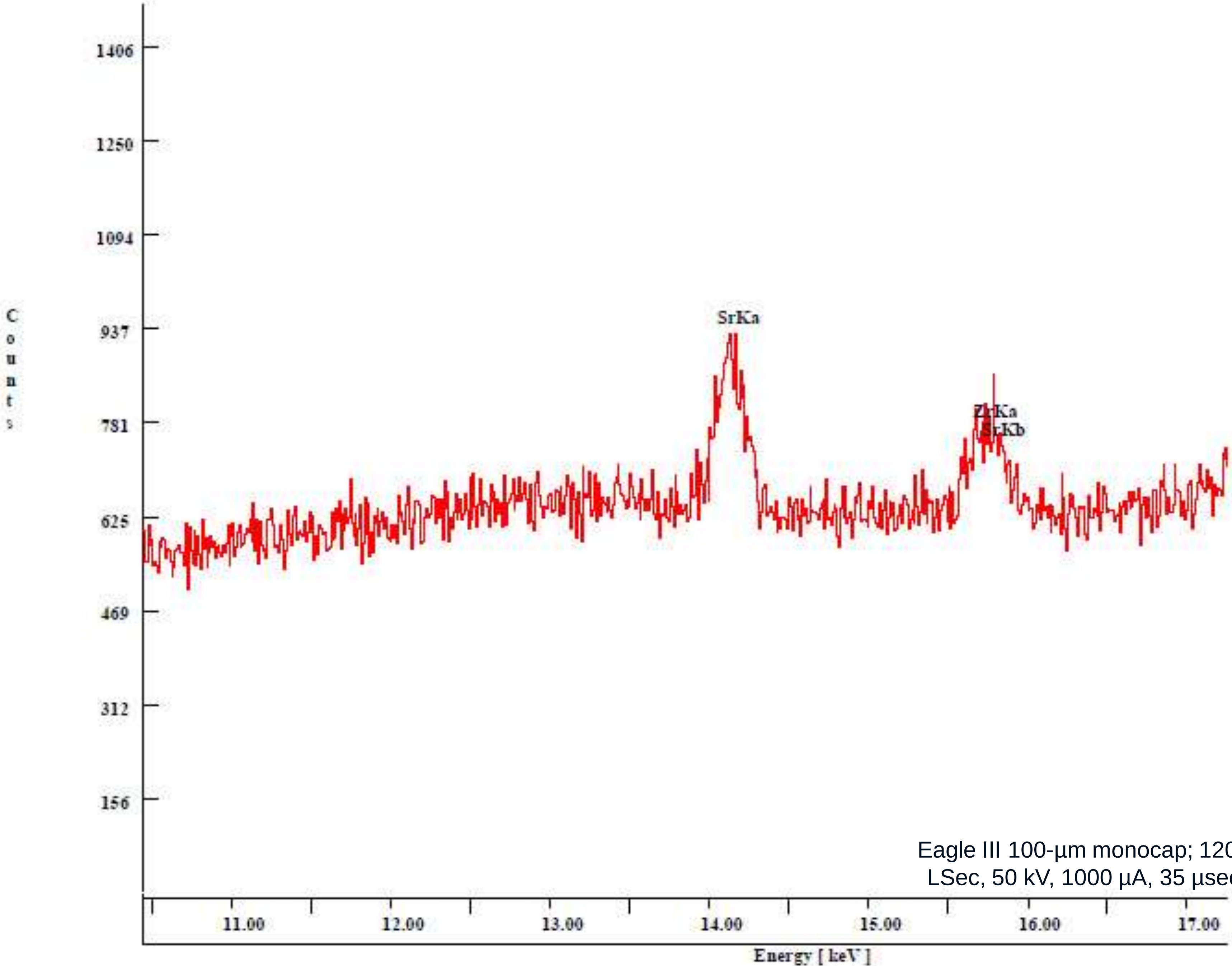
  Calculate LODs on standard glasses
- How does it compare to other systems?

  Compare LODs
- QA/QC:

  Meet LOD or SNR thresholds

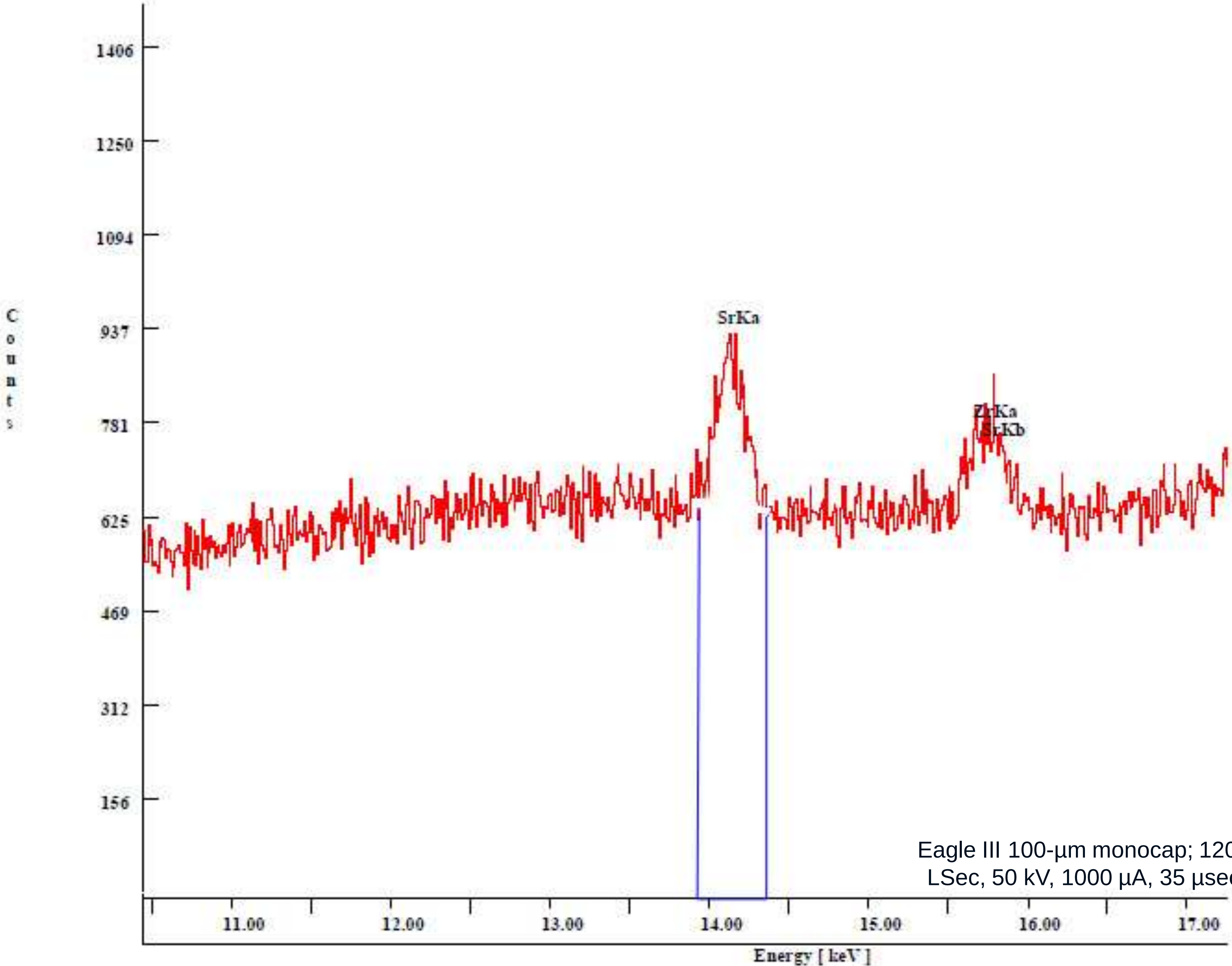
How to Calculate SNRs





Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

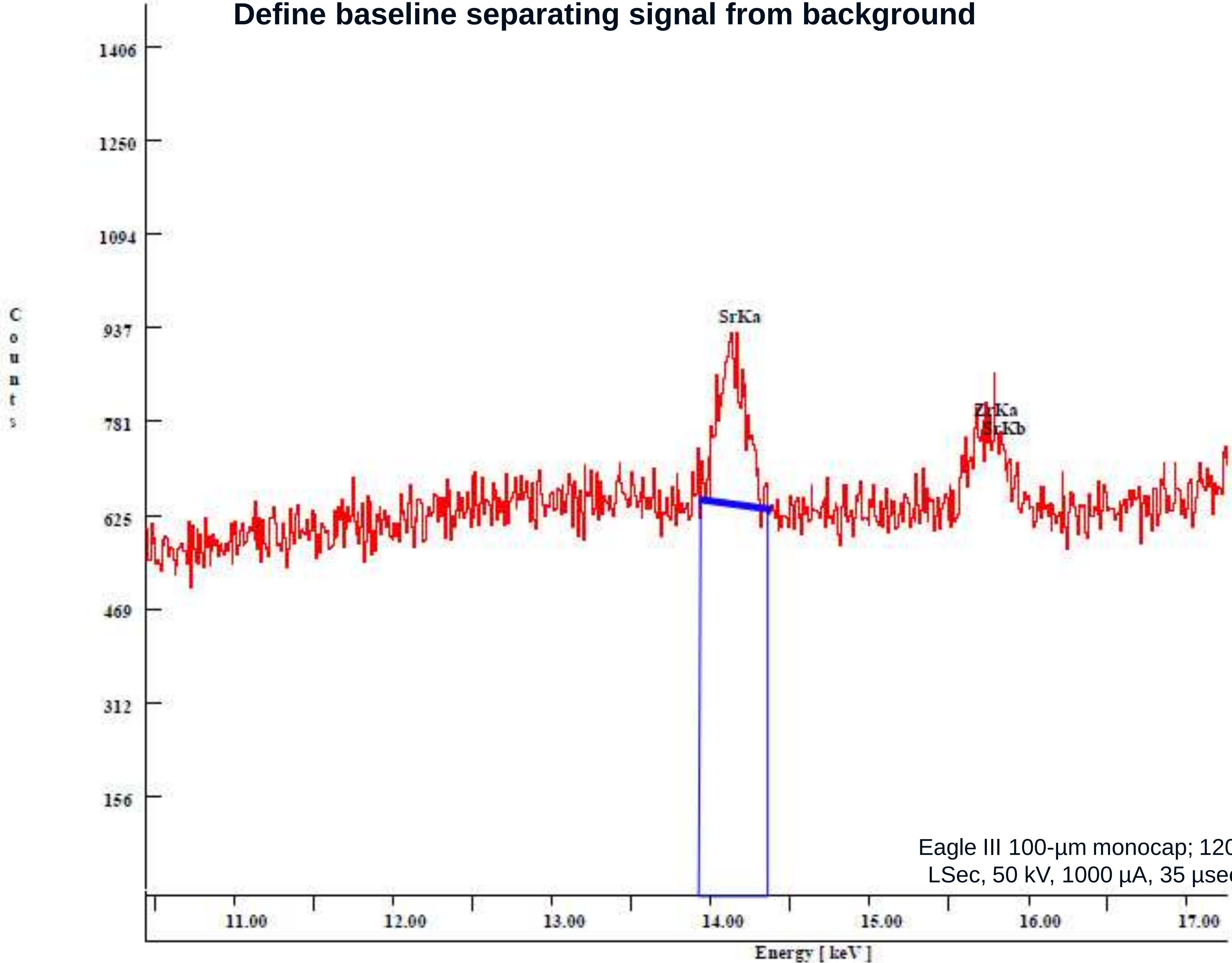
Identify channels of interest: 1394-1434



Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

Identify channels of interest: 1394-1434

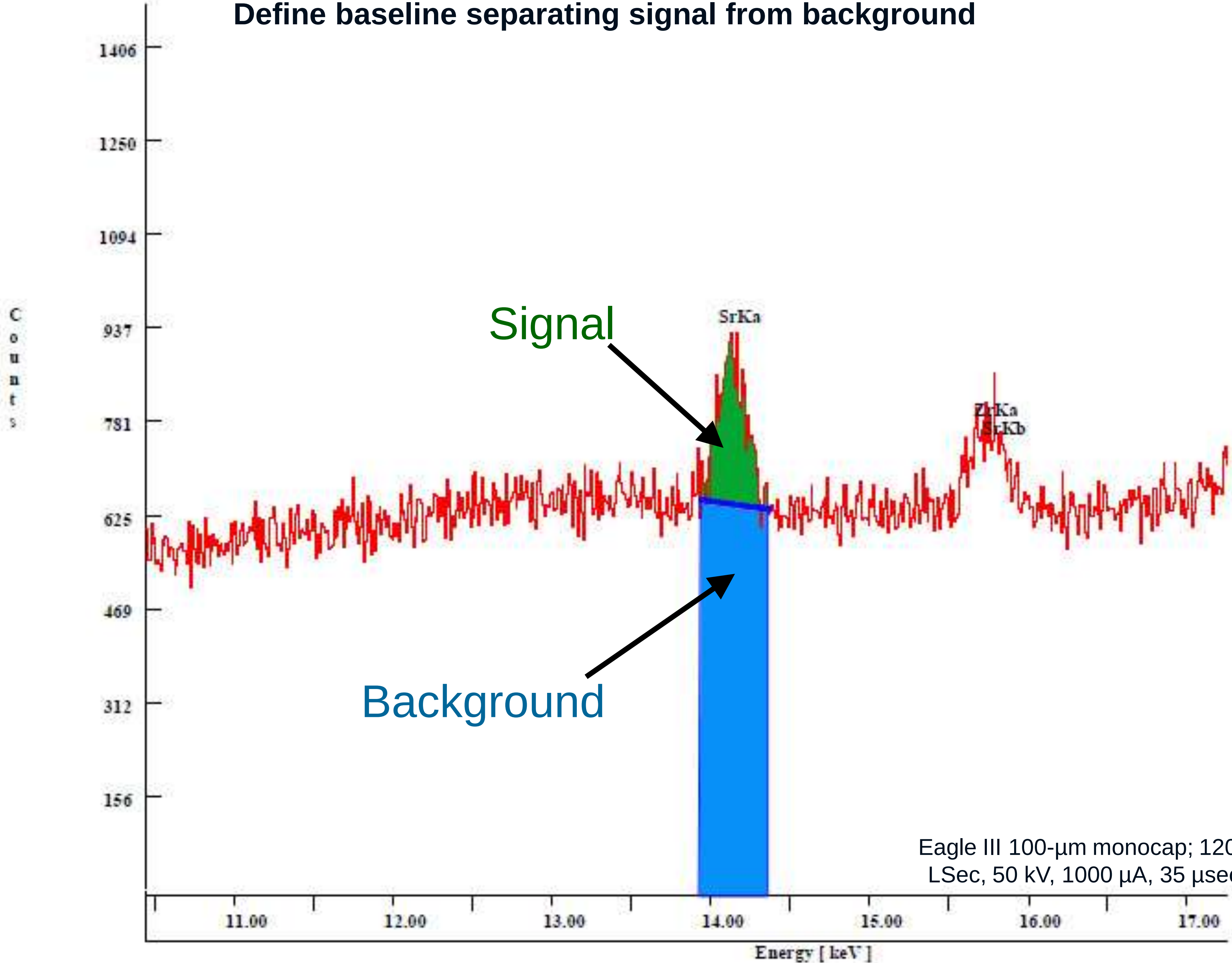
Define baseline separating signal from background



Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

Identify channels of interest: 1394-1434

Define baseline separating signal from background

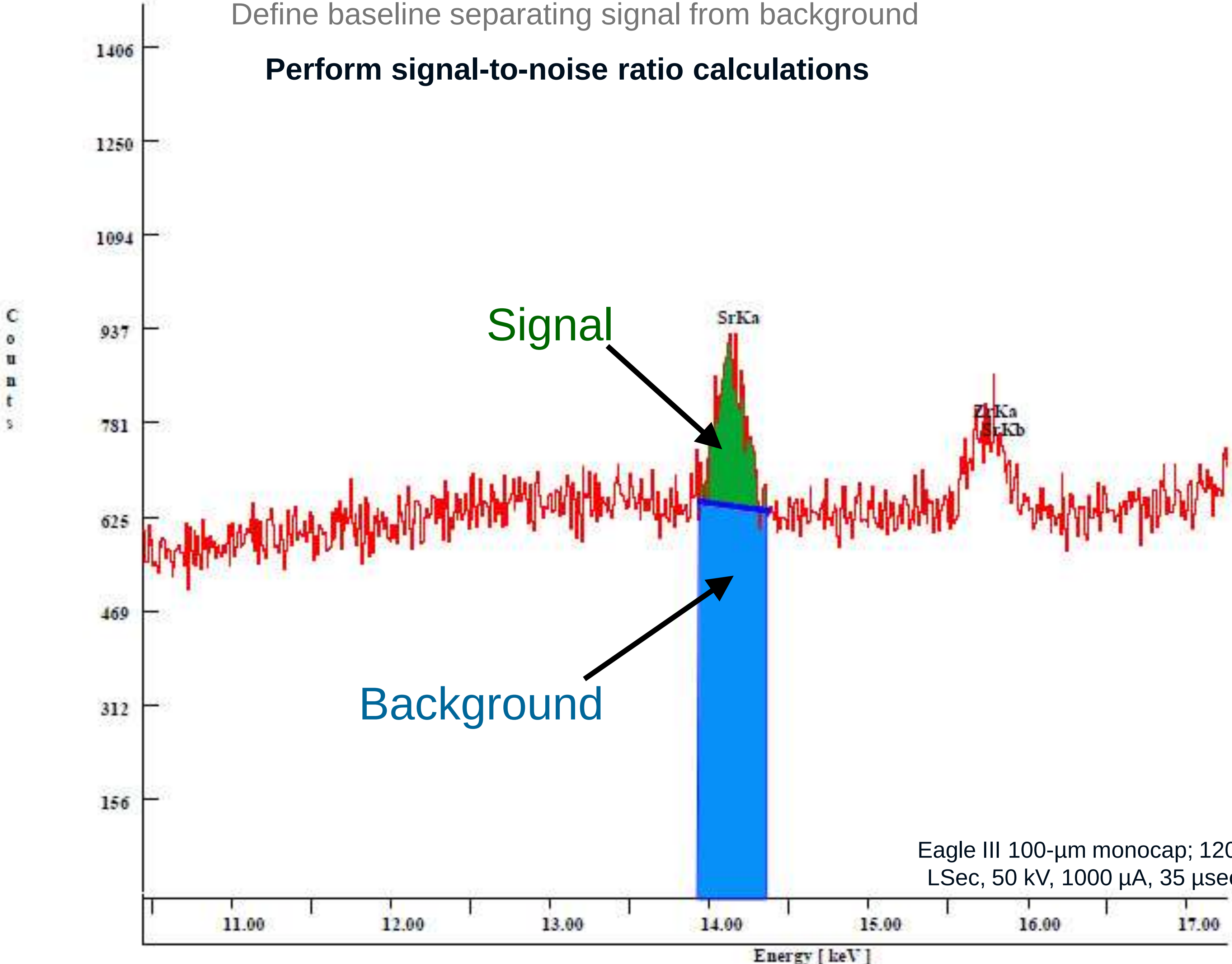


Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

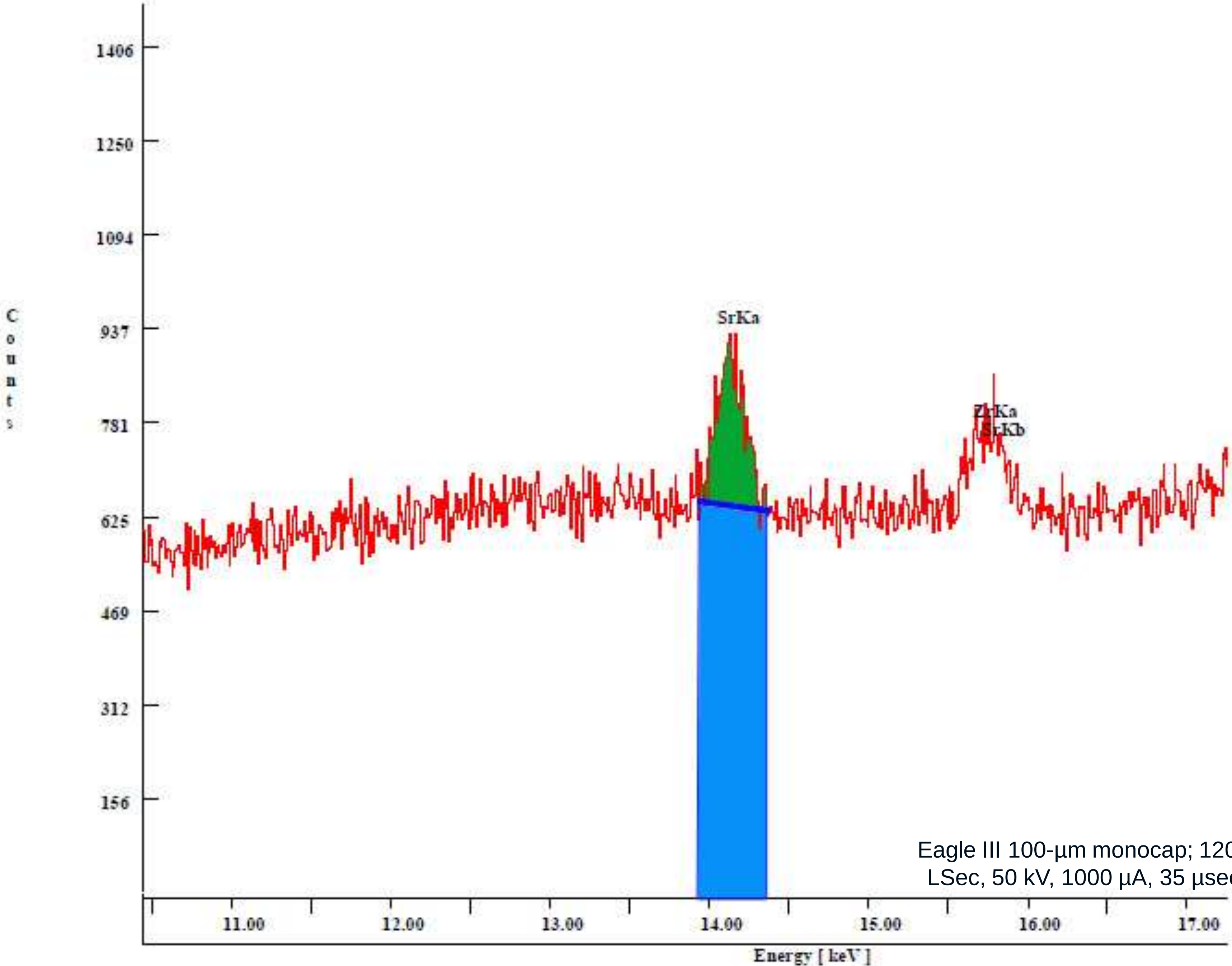
Identify channels of interest: 1394-1434

Define baseline separating signal from background

Perform signal-to-noise ratio calculations



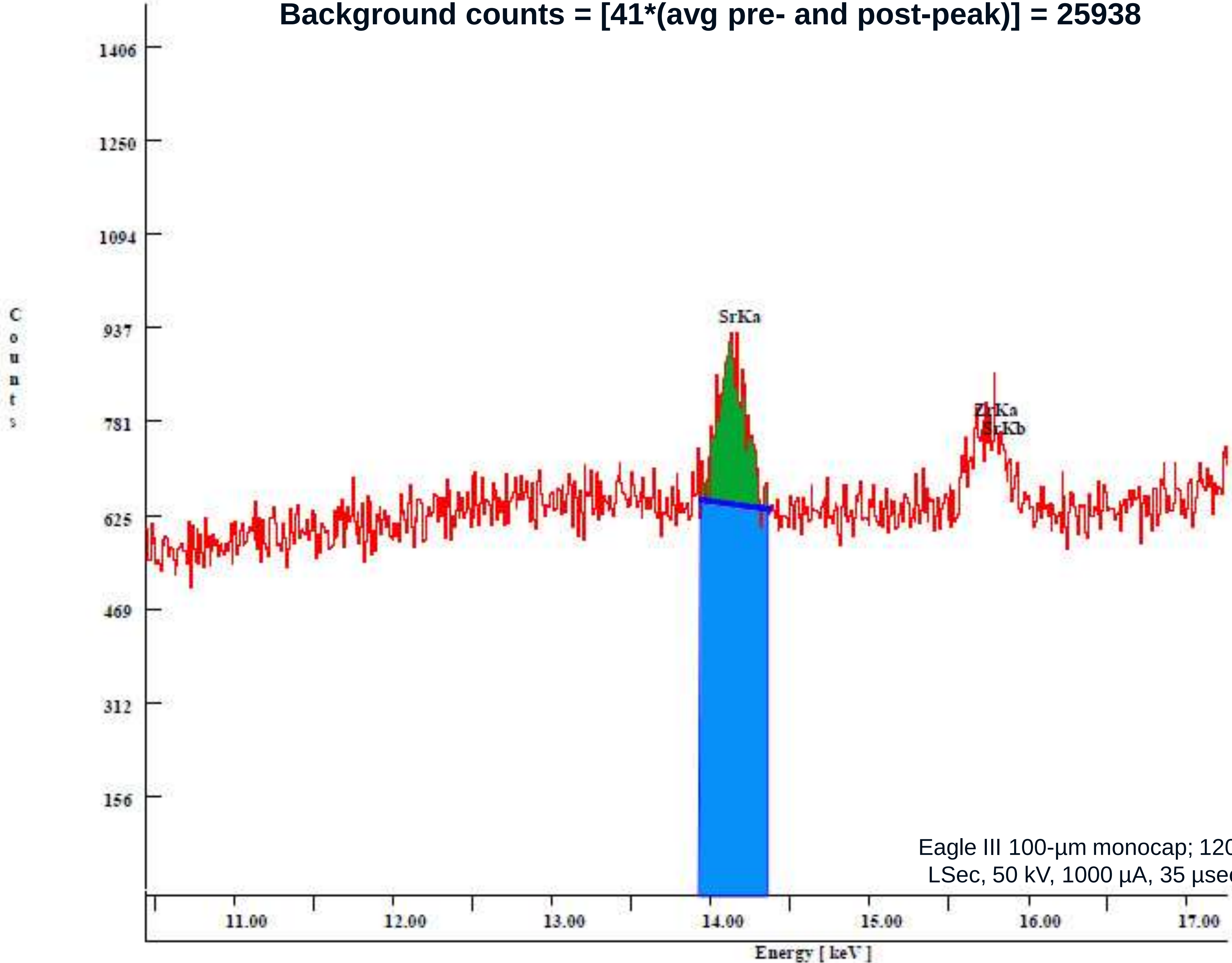
Total counts (channels 1394-1434) = 31797



Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

Total counts (channels 1394-1434) = 31797

Background counts = [41*(avg pre- and post-peak)] = 25938

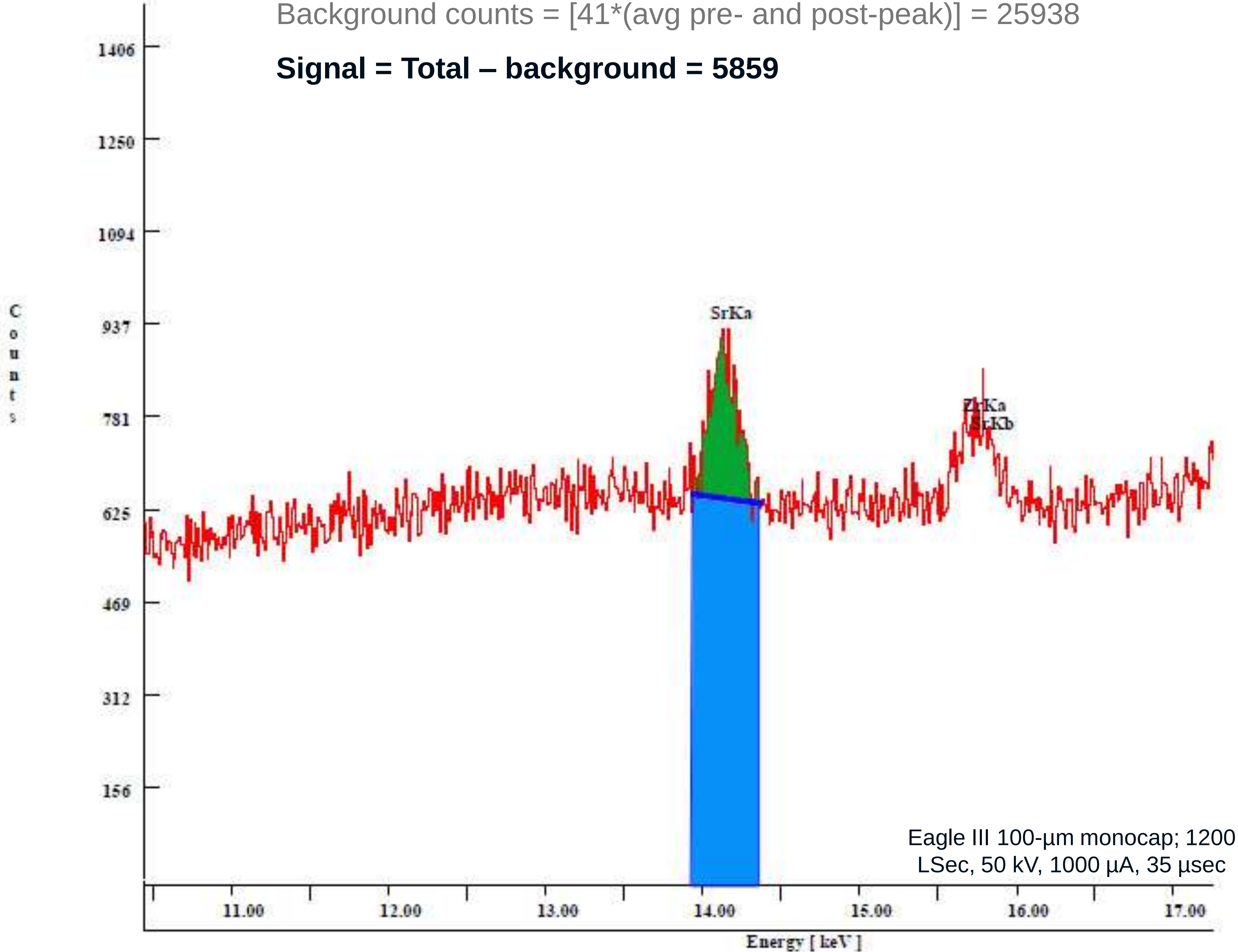


Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

Total counts (channels 1394-1434) = 31797

Background counts = [41*(avg pre- and post-peak)] = 25938

Signal = Total – background = 5859

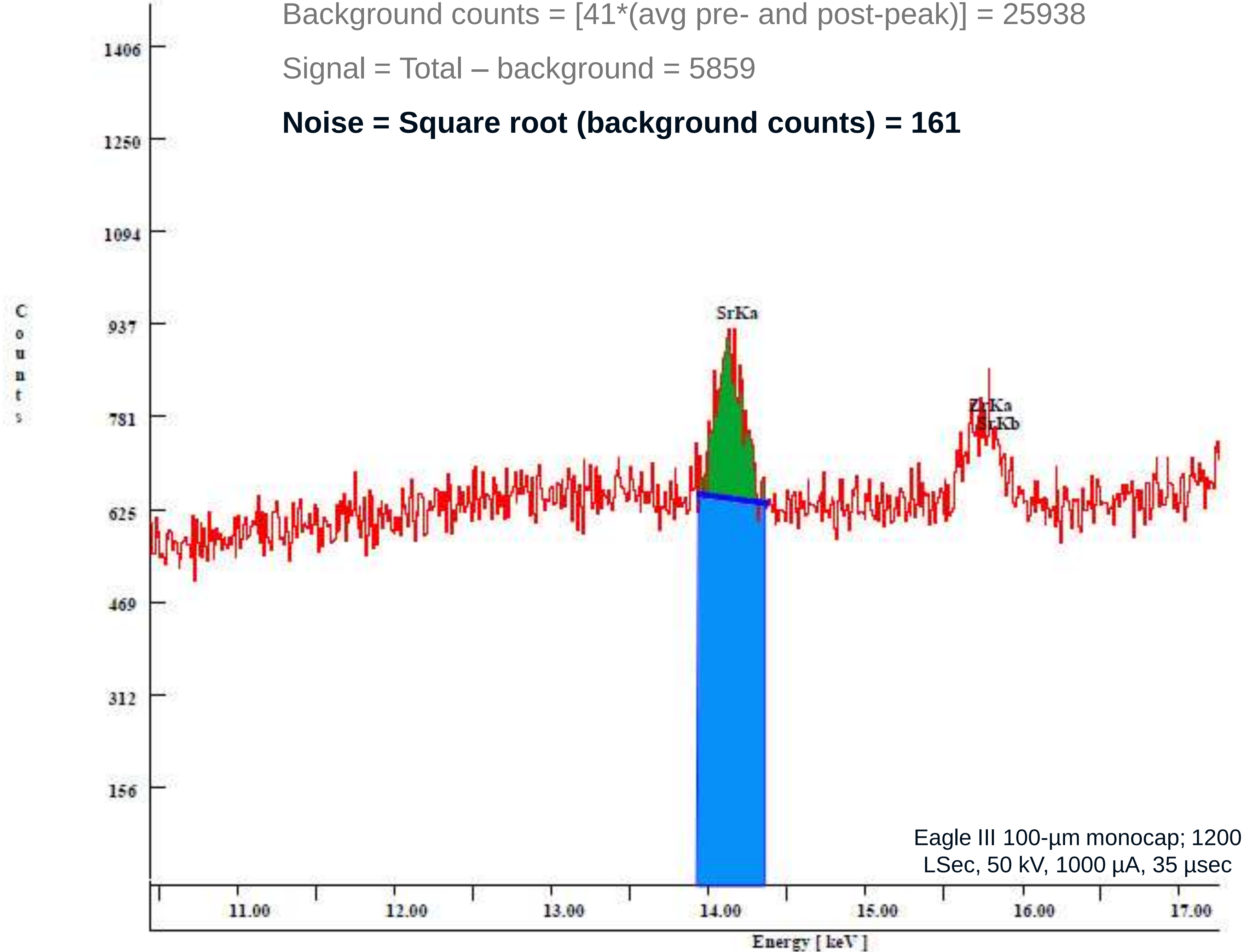


Total counts (channels 1394-1434) = 31797

Background counts = [41*(avg pre- and post-peak)] = 25938

Signal = Total – background = 5859

Noise = Square root (background counts) = 161



Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec

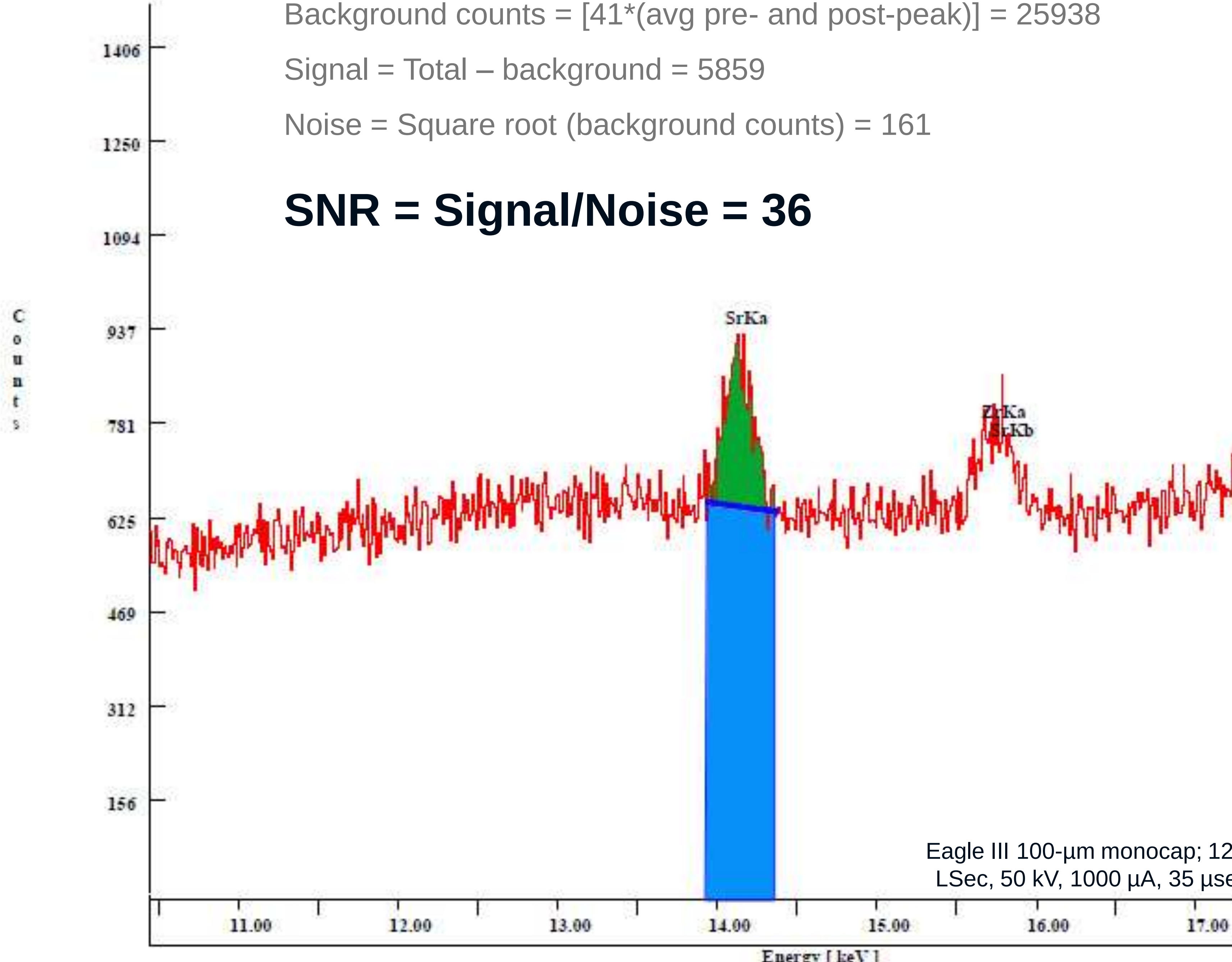
Total counts (channels 1394 -1434) = 31797

Background counts = [41*(avg pre- and post-peak)] = 25938

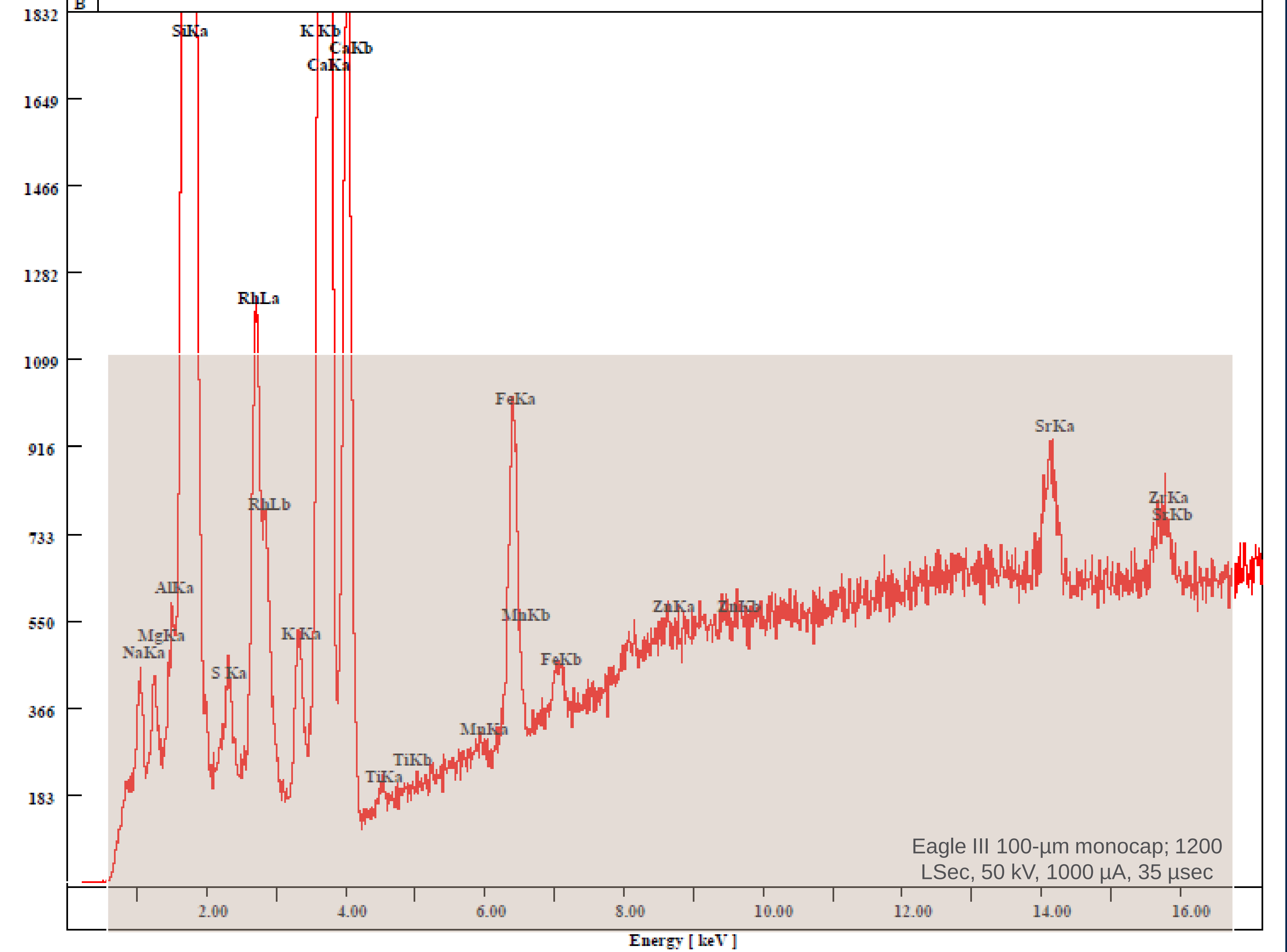
Signal = Total – background = 5859

Noise = Square root (background counts) = 161

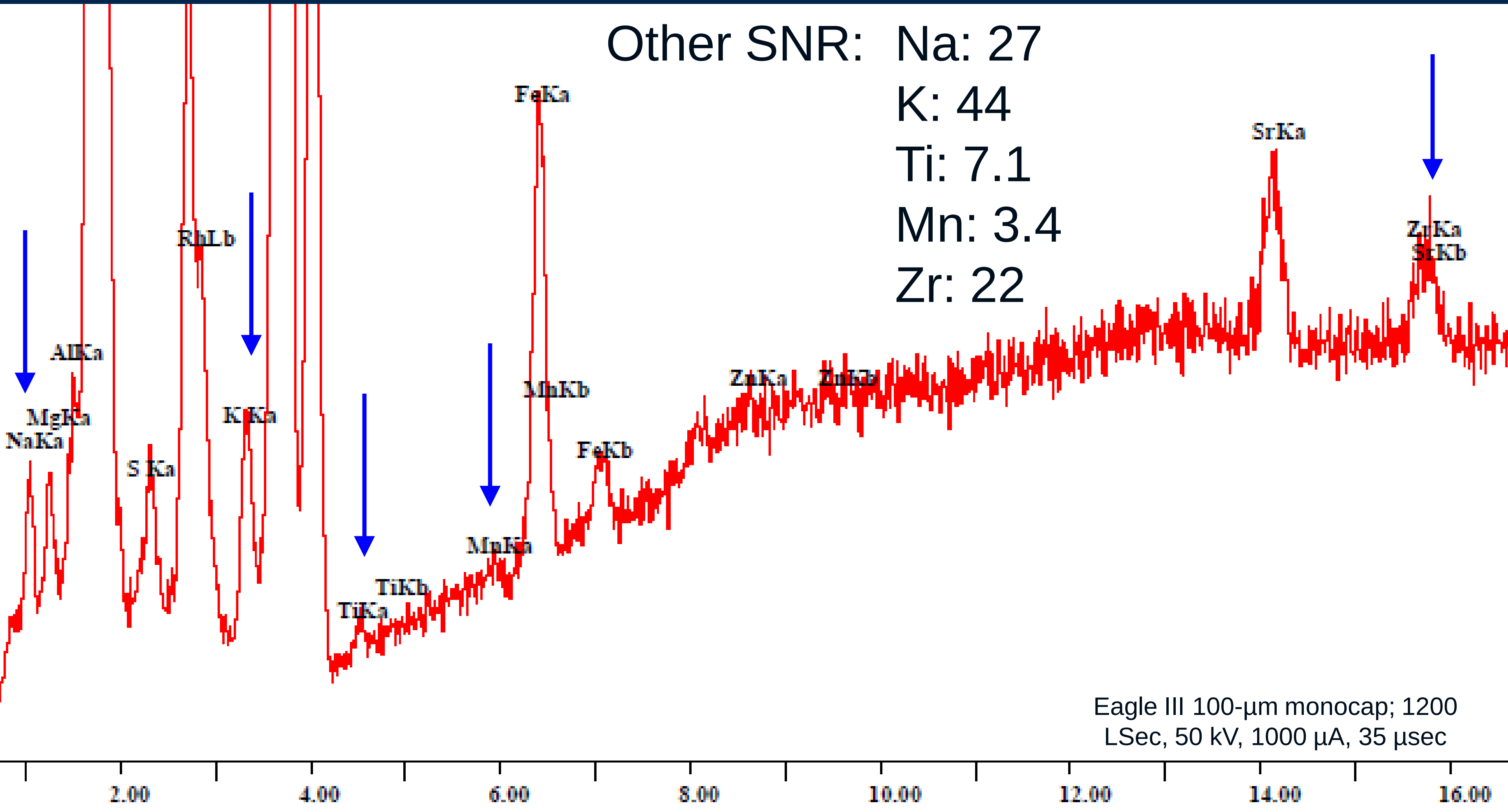
SNR = Signal/Noise = 36



Eagle III 100-µm monocap; 1200 LSec, 50 kV, 1000 µA, 35 µsec



B
1832
1649
1466
1282
1099
916
733
550
366
183
SiKa
K Kb
CaKb
CaKa
RhLa
FeKa
SrKa
ZrKa
SrKb
RhLb
AlKa
MgKa
NaKa
S Ka
K Ka
MnKb
FeKb
ZnKa
ZnKb
MnKa
TiKb
TiKa
Eagle III 100-µm monocap; 1200
LSec, 50 kV, 1000 µA, 35 µsec
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00
Energy [keV]


Other SNR: Na: 27
K: 44
Ti: 7.1
Mn: 3.4
Zr: 22
FeKa
SrKa
ZrKa
SrKb
RhLb
AlKa
MgKa
NaKa
S Ka
K Ka
MnKb
FeKb
ZnKa
ZnKb
MnKa
TiKb
TiKa
Eagle III 100-µm monocap; 1200
LSec, 50 kV, 1000 µA, 35 µsec
2.00
4.00
6.00
8.00
10.00
12.00
14.00
16.00

References

- International Union of Pure and Applied Chemistry (IUPAC), Commission on Spectrochemical and Other Optical Procedures for Analysis, *Pure & Applied Chemistry*, 1976, 45, 99
- ACS Committee on Environmental Improvement, "Guidelines for Data Acquisition and Data Quality Evaluation in Environmental Chemistry," *Analytical Chemistry*, 1980, 52, 2242-2248.

Acknowledgments

- Michigan State Police
- The EAWG members
- NIJ grant to FIU to fund the EAWG effort 2009-DN-BX-K252.

Note: Points of view in this presentation are those of the authors and do not necessarily represent the official position of the U.S. Department of Justice

Thank you

Questions?

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Supplemental Tables

Channel list used in this project

	pre-peak	**Peak range**	post-peak
Na	92-96	**95-113**	112-116
Mg	113-117	**116-134**	133-137
Al	138-142	**142-156**	155-157
S	211-216	**221-241**	246-251
K	314-318*	**321-341***	344-348*
Ca	317-321	**349-389**	424-428
Ti	422-431	**436-466**	471-480
Cr	511-521	**526-556**	561-571
Mn	559-569	**574-604**	609-619
Fe	605-615	**620-660**	665-675
Ni	720-727	**732-762**	767-774
Cu	774-784	**789-819**	824-834
Zn	833-843	**848-878**	883-893
As	1023-1033	**1038-1068**	1073-1083
Rb	1312-1317	**1321-1351**	1355-1360
Sr	1379-1389	**1394-1434**	1439-1449
Zr	1539-1549	**1554-1594**	1599-1609

After the completion of this project, the ranges used for K were modified to 319-322, **325-340**, and 341-344

Average Limits of Detection (ppm) for Configurations A-G

	A	B	C	D	E	F	G
Na	6979	1744	2592	6213		2337	5073
Mg	1587	657	653	1605		655	1264
Al	854		455	823		277	559
K	129	50	67	163	297	23	78
Ca	60	16	28	66	167	16	54
Ti	28	13	11	29	70	9.0	23
Mn	17	7.9	9.2	19	42	6.6	15
Fe	14	5.8	7.9	15	33	6.7	13
Rb	7.0	5.6	4.3	7.7		6.5	7.5
Sr	7.0	5.5	4.5	7.3	9.1	7.1	7.4
Zr	5.4	4.1	3.5	5.6		5.7	5.7

Each value represents the average of the calculated LODs for triplicate measurements on each of three standard glass materials (NIST SRM 1831, FGS-1, and FGS-2). Configurations shown on the next page.

Instrument configurations and parameters

	A	B	C	D	E	F	G
Instrument Type	Stand-alone	Stand-alone	Stand-alone	Stand-alone	SEM add-on	Stand-alone	Stand-alone
Tube Type	Rh	Rh	Rh	Rh	Mo	Rh	Rh
Capillary Type	mono	poly	mono	mono	poly	poly	mono
Spot Size (microns)	100	30	300	100	100	114	100
Energy (kV)	50	50	40	50	45		50
Power (uA)	1000	100	~800	1000			1000
Time Constant (usec)	35	12.6	17	35	2		35
Collection Time (Lsec)	1200	1200	1200	1200	1200	1500	1800